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DETAILED ANALYSIS OF TUBES REMOVED FROM THE PICKERING NGS MODEL HEAT EXCHANGER RIG AFTER VARIOUS EXPOSURE TIMES

Report No 90-115-K

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ABSTRACT

The results of a detailed examination of tubes removed from the moderator heat exchanger rig at the Pickering site revealed information on the fouling sequence and the nature of the localized corrosion. Initially the tubes become covered with a biofilm. Sediment particles attach to this biofilm and act as nuclei for the deposition of a calcareous layer. The establishment of a calcareous layer, together with coincidental sediment build-up leads to the formation of discrete microenvironments at the metal/fouling interface. The result was the formation of pits after fourteen months in the NO8800 tubes. Analysis of the corrosion products in and around the pits suggests that bacteria have a role in the corrosion process.

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EXECUTIVE SUMMARY

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A.M. Brennenstuhl
Corrosion and Tritium Technology Section

The poor corrosion resistance of alloy N08800 heat exchanger tubes at Ontario Hydro's Pickering Nuclear Generating Station led to the initiation of a research program aimed at understanding the problem and alleviating it. A major component of the program included the installation of a model heat exchanger rig at the Pickering site in order to make quantitative comparisons amongst the current alloy and potential replacements. Tubes were removed from the rig, for examination, after exposure periods ranging from a few days to fourteen months. The results indicated that all tubes regardless of their chemical composition became covered with biofilms following placement in the heat exchanger rig. The deposition of a calcareous layer followed biofilm formation. Sediment build-up occurred coincidentally. This resulted in the creation of discrete microenvironments at the metal/fouling interface which influenced the electrochemical reactions occurring in this region. Corrosion pits were observed after fourteen months of exposure on N08800 tubes. Analysis of the corrosion products in and around the pits suggested that bacteria had a role in the corrosion process.

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To Mr. R.W. Patterson
Manager
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DETAILED ANALYSIS OF TUBES REMOVED FROM THE PICKERING NGS MODEL HEAT EXCHANGER RIG AFTER VARIOUS EXPOSURE TIMES

1.0 *INTRODUCTION*

Corrosion of alloy N08800 in lakewater first came to light when leaks were detected in moderator heat exchanger tubes at PNGS-A in 1983. A detailed examination of the tubes indicated that leakage was due to underdeposit corrosion/1/. Further failures at PNGS-B after a relatively short period of operation were a clear indication that alloy N08800 was not suitable for the intended application. Replacement moderator heat exchanger bundles made from N08825 and N08028 alloys are now in service at PNGS. The selection of these alloys was based on laboratory data which indicated improved service over N08800. The method of arriving at this improvement factor for these replacement alloys was, at best, rather crude. Therefore, a need for quantitative corrosion data existed. In order to satisfy this need a heat exchanger tube corrosion research program was initiated.

A major part of the research program was the installation of model heat exchangers at Pickering and Darlington NGS. The rigs are intended to provide a faithful simulation of an operating heat exchanger so that service related data on the fouling and corrosion of tubing in Lake Ontario water can be obtained.

The Pickering facility is managed by Central Production Services (CPS) personnel. Its prime purpose is for obtaining information on electrochemical monitoring, the effects of chemical cleaning, biocide treatments and data on the process of fouling development particularly during the early stages. This is an important function as the possibility of obtaining improved performance from N08800 is still of interest. The Darlington rig has a different role; its purpose is to provide long term information on a variety of candidate replacement materials. The bundles in both rigs are removed after planned periods of operation for detailed examination.

This report presents the results of the examination of a number of tubes taken from the PNGS rig after exposure to simulated heat exchanger conditions for periods of time ranging from several months to over one year. The aim of this study was to obtain information on the sequence of events which leads to the pitting process, thereby extending our knowledge on the process which leads to

tube perforation and leakage. In addition, it was hoped that in spite of the tests being relatively short that data would also be gleaned on the relative performance of the materials under test.

2.0 *SAMPLES SUBMITTED FOR ANALYSIS*

The history of the samples submitted for analyses is given in Table 1. These samples represent short, intermediate and long-term exposures to the simulated heat exchanger environment. The alloy types exposed to the simulated heat exchanger conditions were N08800, N08825, N08028, N06625 and N04400.

TABLE 1

HISTORY OF TUBES REMOVED FOR DETAILED ANALYSIS

Installation	*Removal Date*	*Total Exposure Time*
Feb 9/88	Mar 9/88	1 month
Feb 9/88	Apr 9/88	2 months
Dec/86	Feb/88	14 months

3.0 *ANALYTICAL TECHNIQUES*

3.1 *X-ray Diffraction (XRD)*

X-ray diffraction was the method used to determine the bulk chemistry of inorganic materials, ie, minerals, attached to the surfaces of those tubes exposed to the heat exchanger environment for the longest periods. Deposit was scraped from the tubes and attached to a glass fiber with a balsam adhesive material. Powder diffraction patterns were obtained using monochromatic radiation (CuK_{α}), a nickel filter was utilized to eliminate spectra other than that from the mineral deposit. A Debye Shearrer powder camera was employed to record the diffraction patterns. The Debye halo's were measured in the usual manner. Mineral identification was achieved by comparing the patterns with those in the JCPDS powder diffraction file.

3.2 *Optical Microscopy*

Prior to disturbing the deposit attached to the surfaces of the tubes, photomacrographs were made at magnifications ranging from (1-5)X. Typical and atypical areas on the surfaces of the tubes were recorded.

3.3 *X-ray Photoelectron and Auger Electron Spectroscopy*

X-ray photoelectron spectroscopy (XPS) was used to obtain information from the outer surface (2-3 nm) of the tubes. Elemental data were generated from the surface of samples which were selected for analyses. In some cases deconvolution of the peaks were performed in order to establish the chemical binding of the atoms present. As the methods of deconvolution depend upon the

assumption of a mathematical shape for the peak care was taken in assessing whether the computer output bore any relationship to reality as judged from the experimental situation.

All XPS spectra were generated at the Surface Science Laboratory (University of Western Ontario). A Surface Science XPS-100 facility was used throughout and AlK_{α} radiation (kinetic energy of 1486.6 eV) was utilized during the study. The analysis area ranged from 0.09-0.36 mm^2. The larger area was generally used when information was required from areas which appeared to be visibly homogeneous. The smaller area was selected in situations where discrete areas which appeared different from their surroundings were to be examined. Two (2) scans were made for the broad spectrum and at least eight (8) for the single peaks. In order to minimize spectrum shifts due to charging effects, the samples were covered with a silver grid.

Initially all spectra were generated from undisturbed surfaces. No attempt was made to clean the surface after removal from the rig, so large amounts of carbon and oxygen were expected. Subsequent analyses were performed after lightly sputtering to remove contamination caused by exposure to the laboratory environment. Spectra were obtained once the outermost layer of contamination had been removed.

The XPS examination was performed prior to the Auger and scanning electron microscopy as it is the most passive technique in terms of surface damage.

3.3.1 *Auger Electron Spectroscopy*

Auger electron spectroscopy (AES) was used in conjunction with XPS because of AESs much reduced probe size (lateral resolution of <100 nm versus 150 μm for XPS). This has obvious advantages when examining surfaces which display inhomogeneities such as the heat exchanger tube samples.

The PHI 600 Auger facility at Surface Science Western was used during this investigation. All data were generated with a 10 kV electron beam. Argon sputtering was employed when in-depth information was required.

3.4 *Scanning Electron Microscopy/Energy Dispersive X-ray Analysis*

The scanning electron microscope (SEM) was utilized to examine the topography of the tube surface and to obtain information on the "bulk" composition. Elemental information was obtained with the energy dispersive x-ray analysis (EDXA) system. These analyses were performed after the AES examination to minimize the possibility of electron beam damage to the surface due to the higher electron beam voltage utilized by the SEM. A JEOL 840A SEM and Link Systems AN1000 EDXA facility were used for this examination; an acceleration voltage of 20 kV was employed throughout. All EDXA spectra were deconvoluted (ie, the effect of the instrument measuring resolution was removed) to obtain a best fit and the data were atomic number absorption and fluorescence (ZAF) corrected to acquire semi-quantitative elemental information.

Because generally the surfaces being examined were non-conductive, it was necessary to coat them with gold or carbon prior to insertion in the sample chamber of the microscope. This precaution was taken to eliminate problems associated with the imbalance between the incident (primary electrons) and secondary electrons, ie, charging. Gold was used when topographical information was required but not in situations when it was likely that elemental data were sought. The reason for this was the close proximity of the gold M_α and sulphur L_α lines. When elemental data were to be obtained, carbon was used.

3.5 *Metallography*

When as a result of light microscopy it became apparent that the surface of the tube(s) were pitted (only the N08800 tubes), a section of the alloy which included the pit was removed from the tube. The sample was then mounted in such a way that the depth of the pit(s) could be measured.

3.6 *Defouling*

In order to remove the fairly heavy fouling which was present on the tubes which had been exposed for relatively long periods of time, they were rinsed with 10% formic acid. The formic acid was applied with a wash bottle. Only small areas were cleaned so that if pits were revealed by the cleaning process some fouled areas of the tube would remain undisturbed. This method of inspection made it possible to look for indications of pitting in those areas which had not been cleaned.

4.0 *RESULTS*

4.1 *Macro Examination*

Photomacrographs of the three (3) types of deposit can be seen in Figures 1a-c. It should be noted that the observations made here are common to all of the alloy types examined during this study.

4.1.1 *Short Term Exposures (1-2 months)*

Figure 1a is typical of what was seen during the early part of exposure. The tube surface was coated with a thin uniform golden brown/bronze layer. This layer was well attached to the surface when dry, a sharp implement was necessary to remove it. However, when wet it could be quite easily wiped from the surface.

Exposure of the tubes to the heat exchanger environment for two months led to a change in the colour of the deposit (see Figure 1b). The deposit became a grey/beige colour.

4.1.2 *Long Term Exposure (14 months)*

Eventually after extended exposure, a relatively thick brown deposit which had a course "gritty" texture covered the tubes (see Figure 1c). In addition, pits were occasionally seen on the N08800 tubes. It is worth mentioning that this deposit could be peeled from the tube quite readily, without decrepitation ie, it had good mechanical strength in itself but its adhesion to the tube (actually the biofilm attached to the tube) was poor. The pieces of deposit were carefully stored for later surface analysis.

All of the tubes regardless of their composition, exhibited the stages of fouling development described. However, only the N08800 tubes displayed underdeposit corrosion, and this was confined to the tubes which had been in service for fourteen (14) months. Relatively few pits were seen and they were all very small, (less than 1 mm in diameter and 70 μm deep). It was not possible to locate the pits without first removing the deposit.

4.2 *X-ray Diffraction*

The result of the x-ray diffraction on material removed from the tubes exposed for fourteen months revealed the presence of calcite, dolomite, quartz and feldspar.

4.3 *X-ray Photoelectron and Auger Electron Spectroscopy*

4.3.1 *Short Term Exposure*

Figure 2 is an XPS broad scan from the surface of the sample which had only seen one (1) month of operation. Clearly, the most dominant species at the surface were oxygen (25%) and carbon (66%), also present were relatively large quantities of silicon (2.0%) and nitrogen (4.0%) and small amounts of copper (.3%), iron (1.0%), calcium (0.7%), and sulphur (0.7%). Deconvolution of the carbon line indicated that there were four (4) carbon groups: hydrocarbon, hydroxyl, carbonyl and carboxyl. Figure 3 shows the deconvoluted line and indicates the approximate amounts of each species present. Examination of the nitrogen line (see Figure 4) suggests that ammonium nitrate was also likely present; absolute identification was not possible. Deconvolution of the other lines was not performed because of the relatively low intensities observed for the other species.

An AES spectrum from the same sample can be seen in Figures 5a-c. It should be noted that the data obtained were from a much smaller area than was the case with the XPS study. Figures 5a-5c represent the low energy end of the Auger spectrum only. The high energy part did not reveal any additional information so it has not been included. Prior to sputtering the presence of relatively large quantities of carbon, oxygen, silicon, sulphur and phosphorus were evident. An area adjacent to this was also examined. An almost identical spectrum was obtained except that phosphorous was not seen. Sputtering the surface of the sample for one minute (Figure 5b) resulted in the appearance of nitrogen, calcium and iron in addition to those elements

already recorded and a reduction in the quantity of oxygen. It was noted that the silicon peak was enhanced. Sputtering for a further minute revealed low intensity peaks for the alloying elements in addition to those elements already mentioned. Sputtering for a period of four minutes resulted in increased signals from the alloying elements and a decrease in the amounts of carbon and silicon. After eight minutes of sputtering (Figure 5c), almost all of the golden brown/bronze film had disappeared suggesting that the total film thickness of the "dry" film was approximately 120 nm.

A broad XPS spectrum for the grey/beige coating (prior to sputtering) can be seen in Figure 6. The principle elements were once again carbon (52%) and oxygen (32%) together with smaller quantities of aluminum (3.1%), silicon (6.7%), and nitrogen (2.4%). Sodium and flourine were also detected in small amounts. Sputtering for one (1) minute revealed the presence of calcium, sodium and chromium in addition to those elements already reported. The nickel and chromium peaks were likely from the tube surface rather than the deposit as this sample was badly scratched. In some places the bare metal was visible.

Deconvolution of the most intense lines was not attempted because of the complex chemistry of the deposit. It is doubtful whether such information gleaned would add to the discussion on the mechanism of film formation.
An AES spectrum for the grey/beige deposit can be seen in Figures 7a-b. The spectrum was similar to that generated by XPS. It should be noted that aluminum was observed in the high energy part of the spectrum, but is not shown here. A one minute sputter resulted in stronger calcium and oxygen signals. The intensity of the carbon signal was reduced.

4.3.2 *Long Term Exposure (14 months)*

An XPS spectrum of the thick brown film on tubes exposed to the heat exchanger environment for greater than one (1) year revealed the elements shown in Figure 8. Deconvolution of the individual lines was not attempted because it was considered not to be worthwhile in view of the complex chemistry of the layer.

In addition to examining the various types of fouling seen on the tubes, areas on alloy N08800 which displayed pitting corrosion were also studied. As these local areas examined were usually quite small (<1 mm), auger electron spectroscopy was utilized. The auger spectrum of a dark coloured deposit adjacent to a pit can be seen in Figure 9. It is evident that the main elements were oxygen, carbon, calcium and iron. Small quantities of sulphur, phosphorus and chorine were found.

4.4 *Scanning Electron Microscopy/Energy Dispersive X-ray Analysis*

SEM/EDXA did not reveal any new information on the golden brown/bronze or the beige/grey layers. This is likely due to their being so thin. No evidence of pitting was seen on these samples either. The chemical composition results from the heavy brown deposit can be seen in Table 2. Spectra were collected

from the convex (exterior) and concave (interior) surfaces of samples which had been peeled from the tube surface. It should be noted that the convex surface is in direct contact with lakewater, and the concave surface is in contact with the underlying bronze/brown deposit.

TABLE 2

ANALYSIS OF THE THICK BROWN DEPOSIT FOUND ON THE TUBES EXPOSED TO THE HEAT EXCHANGER ENVIRONMENT FOR 14 MONTHS

	Atomic (%)	
Element	Convex Surface	Concave Surface
Mg	3.6(0.3)	6.7(1.3)
Al	1.7(0.3)	2.9(0.45)
Si	4.7(0.3)	9.4(1.45)
Ca	71.7(5.6)	59.5(2.1)
Fe	16.5(6.5)	19.7(1.9)
S	0.3(0.1)	0.9(0.1)
K	0.8(0.3)	1.0(0.1)
Zn	0.2(0.1)	0.7(0.4)
Ti	--	0.2(0.1)
Mn	0.3(0.14)	0.3(0.2)

Note: Figures in parentheses are standard deviations.

From these data, which represent average values obtained from a total of nine (9) different locations, it is evident that the convex and concave surfaces were quite different. The most obvious difference was the three-fold increase in sulphur on the surface closest to the surface of the metal.

A general view of a typical pit observed in alloy N08800 can be seen in Figure 10. Clearly, those areas where major pits were observed were also surrounded by a smaller number of "secondary pits". On close examination (see Figure 11) the pits were found to be highly crystallographic. Analysis of the film on the surface of the crystallographic facets, (see Table 3) revealed the presence of zinc, manganese, calcium, silicon, aluminum, sulphur, potassium and chlorine together with the alloying elements found in alloy N08800. As the film on the facets appeared to be very thin it is believed that the spectrum presented here represents a combination of information from the film and the underlying substrate.

TABLE 3

COMPOSITION OF CORROSION PRODUCT FILMS ON CRYSTALLOGRAPHIC FACETS AND IN SECONDARY PITS

	ATOM. % OF ELEMENT	
ELEMENT	*FILM ON FACETS*	*DEPOSIT IN "SECONDARY PITS"*
Fe	32.9	16.9
Ni	25.9	10.74
Zn	0.2	0.1
Mn	0.6	0.0
Ca	2.5	9.5
Si	1.6	2.7
Al	0.9	3.5
S	0.4	1.3
K	1.0	1.4
P	0.1	0.0
Cl	1.4	1.7
Cr	31.3	49.41
Ti	1.0	2.7

The elemental data generated from some of the "secondary" pits can also be seen in Table 3. It is evident that the corrosion product in these smaller pits was rich in chromium relative to the other alloying additions. This suggests that under the conditions which exist at the fouling/metal interface the solubility of chromium bearing corrosion products is lower than the other alloying elements contained in alloy N08800. It also appears that sulphur and chlorine were present at moderately elevated levels in the secondary pits; as were aluminum, calcium, silicon, titanium, zinc and potassium.

4.5 *Metallography*

Microsections through the pits indicated that there were none greater than 70 μm deep. There was no evidence of undercutting.

5.0 *DISCUSSION*

The object of this examination was to extend our knowledge of the sequence of events which lead to heat exchanger perforation and leakage, and to ascertain whether any of the other candidate materials offer superior performance compared to alloy N08800.

5.1 *Fouling Sequence*

5.1.1 *Biofilm Development*

As a result of the detailed surface analyses of samples which were exposed to the simulated heat exchanger environment for short periods of time, it is evident that an organic film forms on the tubes first, regardless of their

alloy composition. This came as no great surprise, and was suggested by Sharpe/2/ and has been observed by other workers investigating similar problems elsewhere/3/. The results of the analyses performed by Dunstall on various tubes removed from the Pickering test rig revealed the presence of bacteria in this film. It can therefore be classified as a biofilm. The data showed that microbes colonize metal surfaces within days following exposure to lakewater/4/. Figure 12 gives the numbers and types of bacteria that were found. The presence of sulphate reducing bacteria (SRB) should be noted. These microbes have been implicated in the corrosion of austenitic alloys/5,6/. The presence of these bacteria in the biofilm does not necessarily mean that they are active. Only when the redox potential is less than -100 mV/7/ will they multiply and excrete metabolates (hydrogen sulphide and organic acids) which could be corrosive. The biofilm also contains large numbers of aerobic heterotrophs and pseudomonads. Aerobic bacteria are of considerable importance because they excrete large quantities of extracellular polymeric substances (EPS). These are generally compounds which contain sugars and having a sticky nature they encourage sediment particles to attach to the tube surface. Extracellular polymeric substances not only change the physical and chemical environment at the tube interface, they have also been reported to change the cathode kinetics in favour of corrosion. Initially aerobic micro-organisms will be the most dominant bacteria in the film. These bacteria very effectively limit the oxygen supply to the metal surface. In addition gradual film thickening reduces access of oxygen to the metal surface. As a consequence areas beneath the biofilm at the metal surface will become oxygen depleted. This leads to the activation of anaerobic bacteria. The coexistence of oxygen rich and oxygen depleted regions will lead to the formation of an oxygen corrosion cell if the conditions are extreme enough.

No evidence of pitting was found on the tubes which displayed the presence of biofilm only. Work by Sharpe et al. has indicated that the presence of a biofilm alone does not lead to localized anodic activity of alloy N08800 after fourteen months (14) of exposure to lakewater at 25°C/8/. Only when a combination of deposit and biofilm are present are differences in the surface chemistry of the alloy evident after the time indicated.

XPS/AES revealed a number of elemental species in the biofilm, in addition to the expected carbon, nitrogen and oxygen. The detection of sulphur was not a surprising discovery. What was of interest was the type of chemical binding. Unfortunately, deconvolution of the sulphur spectrum was not possible. The peak was too small to obtain reliable data and as a consequence, identification of the exact chemical state of the sulphur seen in the biofilm was therefore not possible. However, the presence of sulphate and all of its reduced forms can be speculated as follows:

1. Sulphate is present in lakewater. Lake Ontario water contains approximately 35 ppm sulphate, the bulk of which comes from pyrite sediments.

2. Sulphate reducing bacteria produce ^{-}HS, S, H_2S and FeS. They also contain approximately 1.5% wt of sulphur/7/.

3. Leakage of thiosulphate and tetrathionate from sulphate reducing bacteria is also possible.

Other elements found in the biofilm were phosphorus, iron, silicon and calcium. The presence of phosphorus, while not always detected, was not surprising as it is found where living matter exists. Inverson/9/ has suggested that volatile phosphorus compounds may be associated with microbiologically influenced corrosion (MIC). Its presence could therefore be important. Silicon may be present as sediment particles trapped in the biofilm, although if this was the case one might expect to see other mineral constituents which with the exception of calcium were not present. Another possible explanation for the silicon may be the presence of fragments of diatom frustules. The obvious sources of calcium are calcium carbonate from the lakewater and the bacteria themselves. Calcium is required for the growth of many, and probably all, bacterial species. Iron is a major constituent in Lake Ontario water. Its major origin is from pyrite sediments.

5.1.2 *Calcareous Material Deposition*

Based on the observations made during this investigation it would appear that the build-up of calcareous material has some difficulty nucleating and growing on the biofilm. This may be related to the pH of the EPS films. It is proposed that its deposition is initiated on mineral particles which have become trapped in the biofilm. Why these particles initiate deposition is unclear as intuitively one might expect that they would also be covered in a biofilm. A possible explanation is that the structure and composition of the biofilm on the sediment particles is different because the substrate is unlike the oxide on the surface of a heat exchanger tube. Initiation occurs by lateral growth and bridging of the individual mineral deposit grains. The result is a semi-continuous calcareous film. Visual examination and scanning electron microscopy of the film indicates that in the early stages it is observed to be very defective in terms of coverage. Presumably, as the film becomes thicker with time, the defect density is reduced. This means that discrete areas of differing electrochemical behaviour will exist.

As a temperature gradient exists along the length of the tube, the growth rate of the calcareous material will vary from one location to the next. Deposition should be greatest at the hot end due to the inverse solubility of calcium carbonate. Differences are not reported, because this aspect of deposition was not investigated. Seasonal variations in the quantity of carbon dioxide dissolved in lakewater will also be a factor in the quantity of calcium carbonate deposited/10/.

5.1.3 *Sediment Deposition*

The surface analyses suggest that sediment is deposited at all stages of the scale formation process because it is almost always present. Energy dispersive data from the convex and concave surfaces of deposits revealed some interesting differences in the composition at these locations. One of the largest differences and possibly quite significant is that of sulphur. On the

concave surface the concentration is three (3) times greater than on the convex side. A possible explanation for this is the formation of insoluble sulphur species by the SRB. The larger quantity of iron on the concave surface seems to support this idea. It is suggested iron ions react with hydrogen sulphide to form iron sulphide. The presence of higher concentrations of elements normally associated with lake minerals (except calcium), on the concave surface is consistent with the idea that calcium carbonate deposition occurs on sediment particles.

One factor which will have an impact on the extent of sediment deposition will be the condition of the lake. During the winter months, the additional turbulence in the lake will lead to a larger volume of suspended particles and as a consequence one might expect greater sediment build-up.

5.1.4 *Pit Formation*

When a stable layer has become established underdeposit corrosion ensues, at least this is the case with alloy N08800 and may also be the situation with the other alloys after longer incubation times. Examination of the corrosion pits clearly showed them to be crystallographic indicating that dissolution was activation controlled, ie, access of donor and acceptor ions was not limited. Analyses of the corrosion products in the pits revealed the presence of the constituents of the alloy together with relatively large quantities of sulphur and chlorine. Generally more of the latter species was observed. The presence of chlorine in relatively high quantities is often implicated in the corrosion process. The substantial quantities of calcium, aluminum and potassium also detected are believed to be of little significance, as their relative concentrations are no different from what is normally seen on the surface of the tubes. Analysis of the film in the immediate vicinity of the pits suggested that it was a mixture of corrosion product organic and calcareous material together with sulphur, phosphorous and iron. Only very rarely was chlorine present in detectable quantities.

5.2 *Mechanism of Corrosion of Heat Exchangers*

This investigation together with the data presented by the Biological Research Section/4/ has provided new information which has helped us to better understand what is happening at the surface of heat exchanger tubes and what the important interactions which lead to corrosion are likely to be. The analyses have indicated that calcareous material is not immediately deposited on the tubes. The entrapment of sediment particles in the "sticky" extracelluar polymeric substance excreted by the bacteria in the biofilm is likely a precursor to deposition. The gradual build-up of a layer comprised of a mixture of biofilm, calcareous material and sediment restricts access of oxygen to the tube surface. Oxygen is essential for the continued maintenance of the protective oxide layer. The result is the formation of a discrete microenvironment at the metal/biofilm interface. Further, the enhanced sulphur and sometimes phosphorous values at the tube surface tend to suggest that bacteria may have a direct involvement in the corrosion process. Recent work in the laboratory (unpublished) involving exposing alloy N08800 to

culture medium inoculated with SRB removed from heat exchanger tubes, indicates that they are capable of encouraging pit formation of this alloy. The tests were carried out using only anaerobic bacteria which means that pitting is possible at very low redox potentials (<100 mV). This observation is supported by electrochemical noise studies on alloy NO8800 samples immersed in freshwater/11/. Intuitively the corrosion of this type of alloy would not be expected under the reducing conditions which prevail when sulphate reducing bacteria are active. However, the environment produced by the SRB is not defined, meaning that the metabolites are not known. It is possible that in addition to hydrogen sulphide reduced forms of sulphate may also be present and that they may result in localized corrosion at low redox potentials. The aggressive effects of thiosulphate ions have been reported in relation to stainless steels and nickel based alloys/12/. It should also be pointed out from the composition of the corrosion product found within the pits and in the area immediately surrounding the pitted region, that a combination of bacteria (S, P metabolites) and lakewater (S and Cl) are likely necessary for corrosion to occur. Further work aimed at determining the exact role of bacteria other than in assisting in deposit build-up is underway.

Whatever the mechanism of oxide breakdown, it is likely to be similar for all of the alloys examined during this investigation as they are all materials which rely on the formation of a passive film to prevent corrosion. The observation that the other candidate materials displayed superior resistance to attack may only mean that the time to pit initiation has been extended. Tapping has shown that these alloys will pit under laboratory simulated conditions/13/ and microbial studies by Dowling/14/ on super stainless alloys suggest that the standard methods of materials selection may not be appropriate.Longer exposures to simulated heat exchanger conditions will provide information on how much service we can expect out of current replacement alloys.

6.0 *CONCLUSIONS*

Heat exchanger tubes installed in a model heat exchanger rig at Pickering NGS quickly became coated with a biofilm. Aerobic heterotrophs, pseudomonads, actinomycetes and sulphate reducing bacteria were identified as the main types of bacteria existing in the film. The biofilm encourages the attachment of sediment particles to the film and is believed to be a precursor to the deposition of a porous calcareous deposit.

Under-deposit corrosion of the NO8800 tubes occurred after approximately fourteen (14) months of exposure to the simulated heat exchanger environment. This was the only alloy to exhibit localized attack suggesting that all of the other alloys were more resistant to this form of corrosion.

The presence of phosphorus and sulphur in the region immediately outside of the pits indicates that bacteria may have a direct role in the corrosion process. However, the detection of relatively large quantities of chlorine within the pits suggests that lakewater chloride is also important.

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Figure 1a

Uniform golden brown/ bronze layer seen on the tube with one month of exposure

Figure 1b

Grey/beige deposit which started to develop after two months exposure

Figure 1c

The thick brown deposit observed after fourteen months

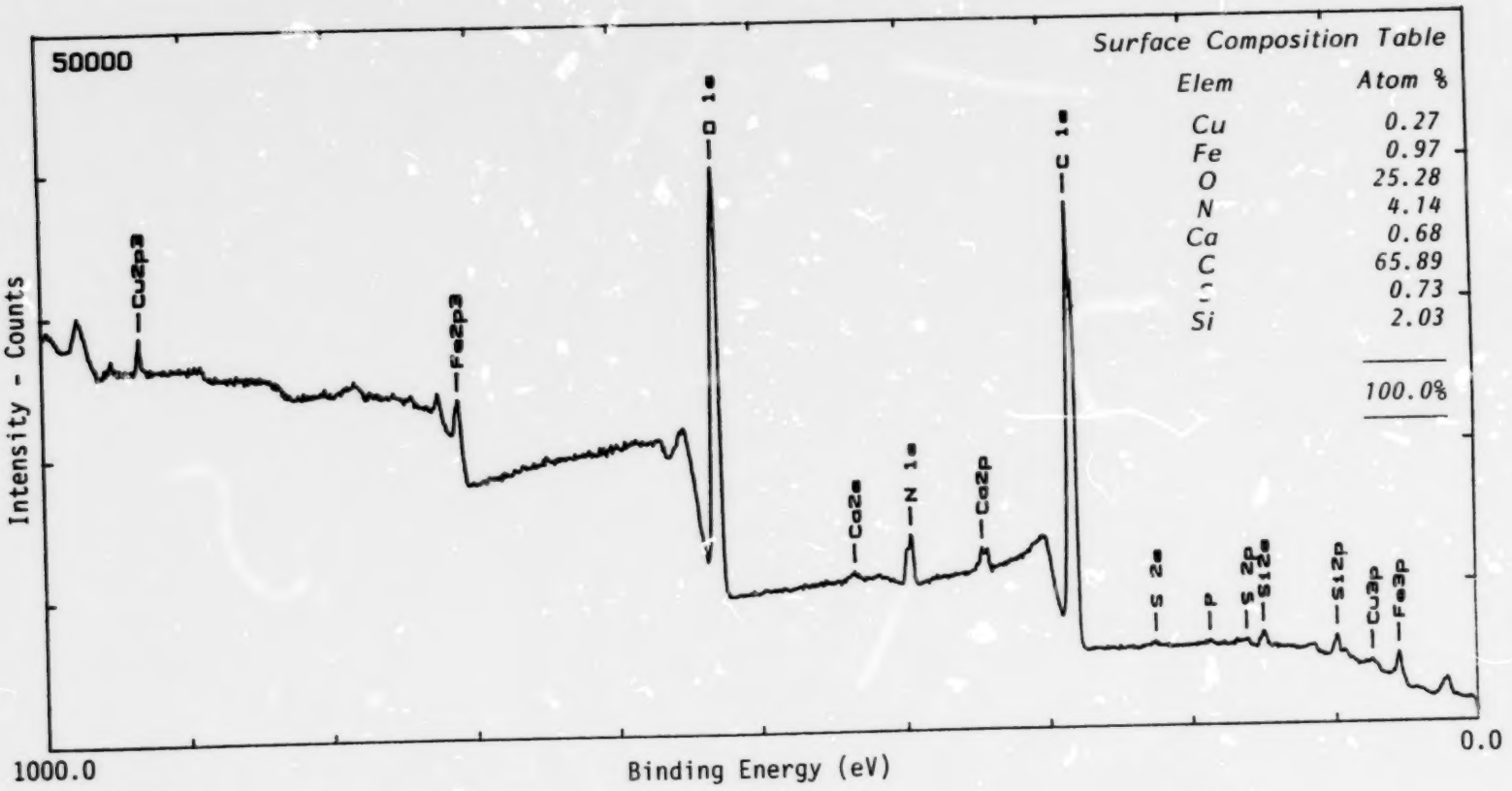


FIGURE 2

AN XPS BROAD SCAN FROM THE TUBE EXPOSED TO THE HEAT EXCHANGER ENVIRONMENT FOR ONE MONTH

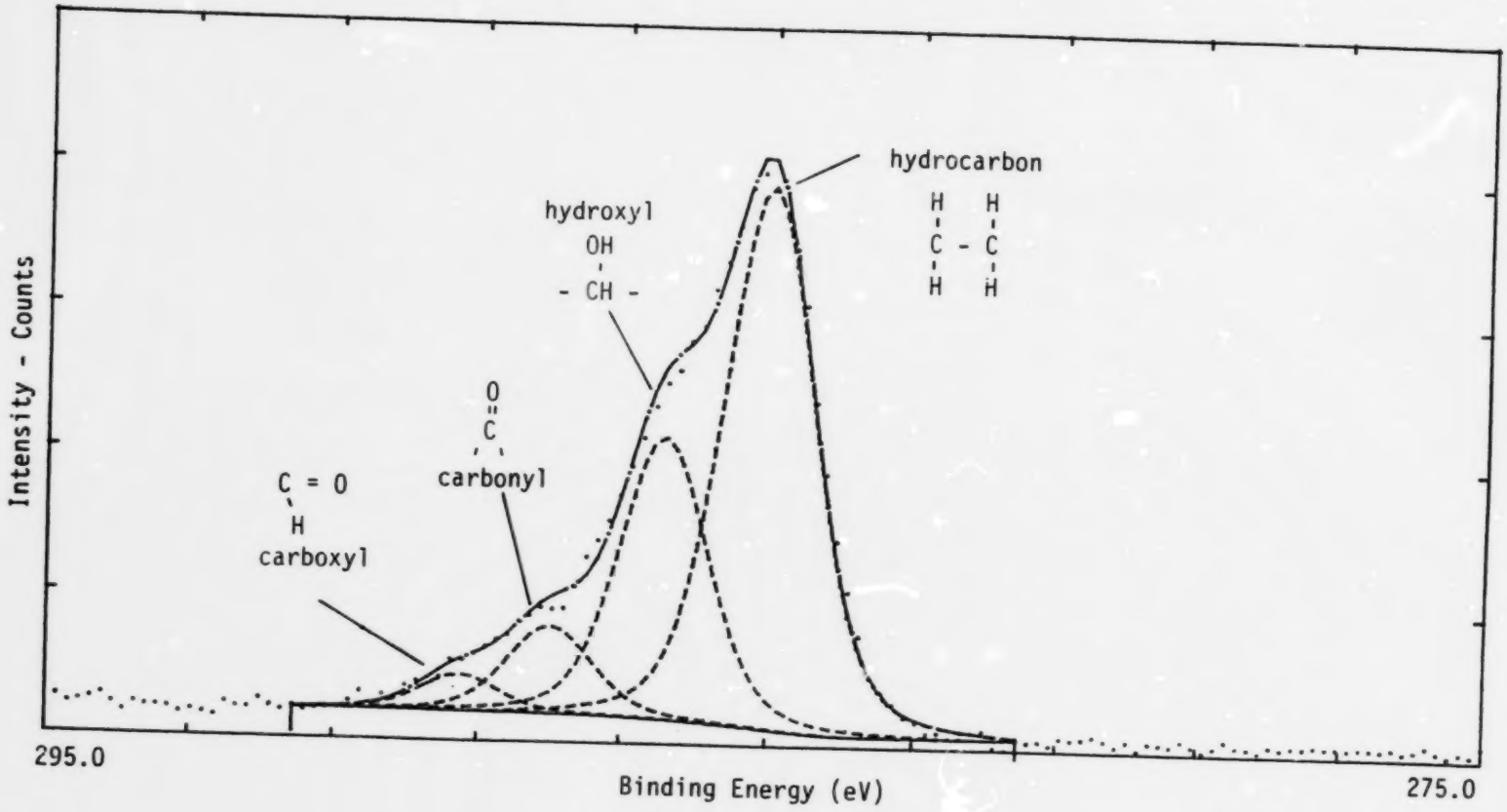


FIGURE 3

DECONVOLUTED CARBON PEAK FROM THE TUBE EXPOSED TO THE HEAT EXCHANGER ENVIRONMENT FOR ONE MONTH SEVERAL CARBON SPECIES ARE PRESENT

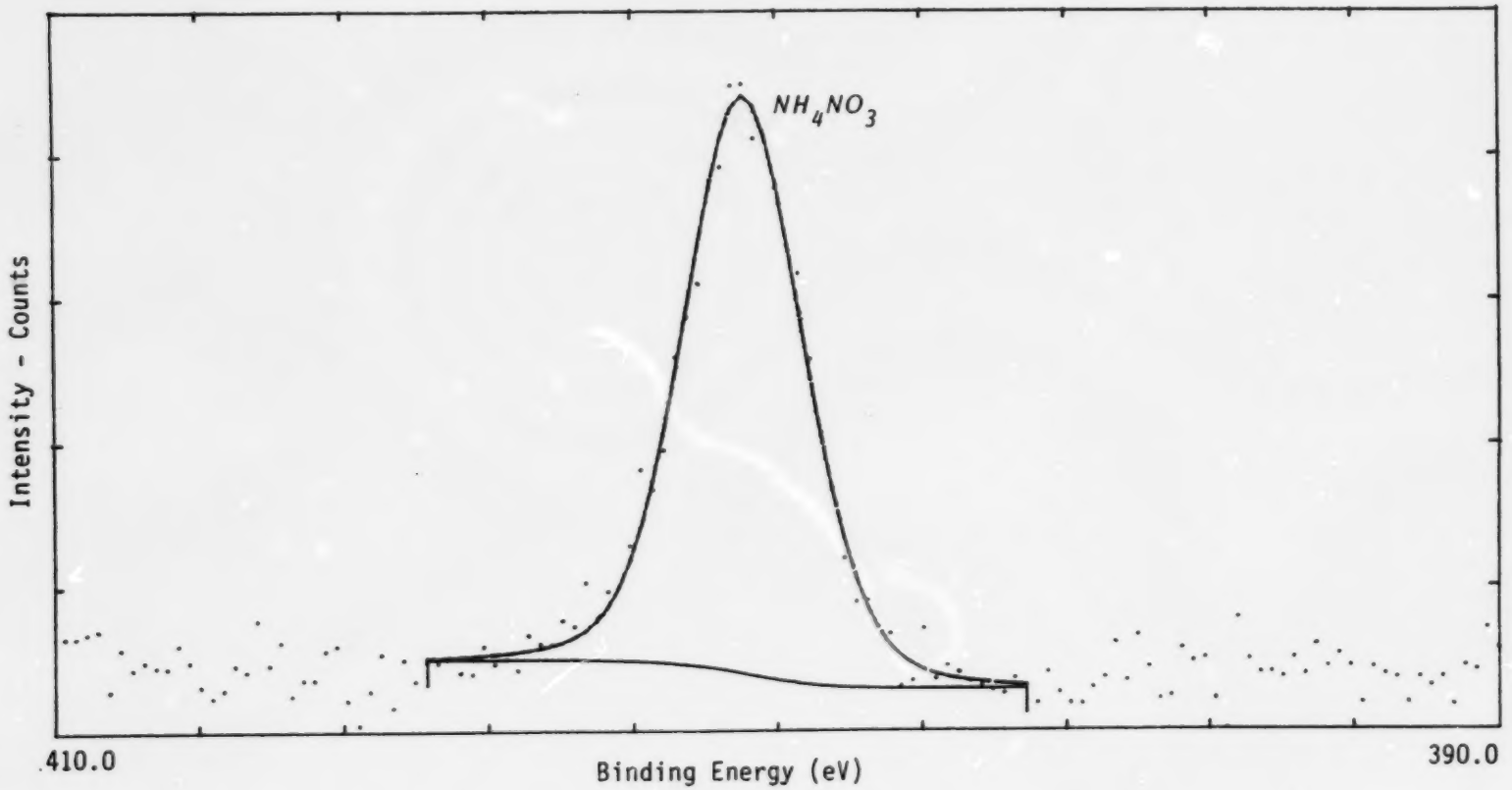
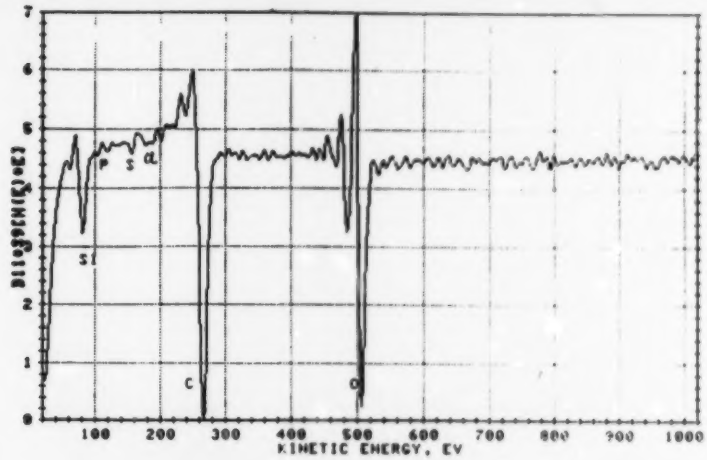
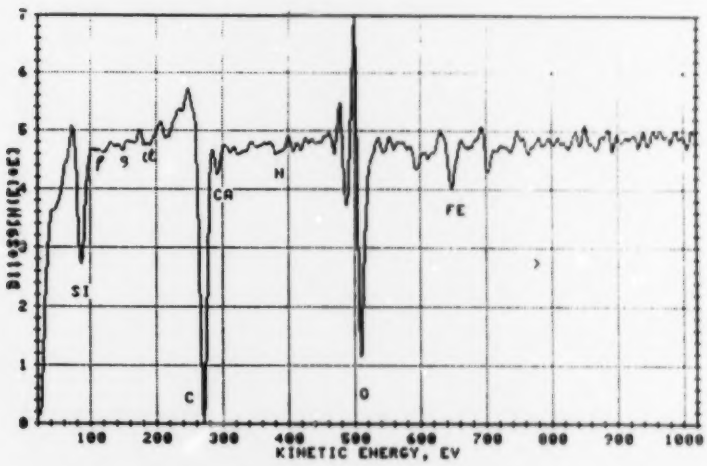


FIGURE 4

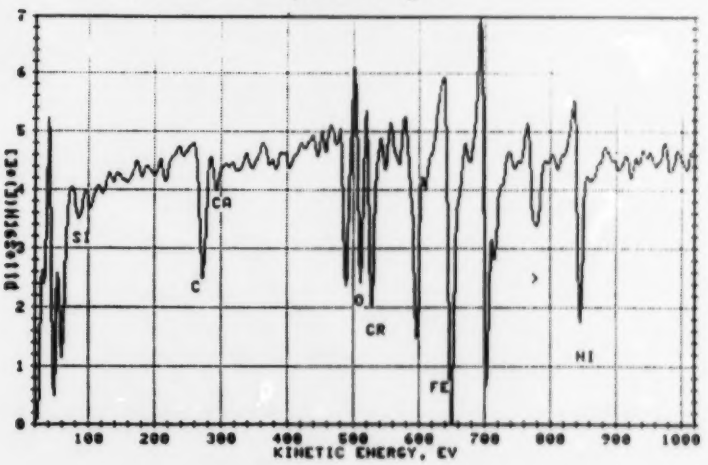
NITROGEN PEAK FROM THE TUBE EXPOSED TO THE HEAT EXCHANGER ENVIRONMENT FOR ONE MONTH THE BINDING ENERGY SUGGESTS THAT NITROGEN IS PRESENT AS NH_4NO_3



(a) Before sputtering



(b) After the removal of ≃ 150A of material (1 minute sputtering)



(c) After the removal of ≃ 1200Å of material (8 minutes sputtering)

FIGURE 5 a-c

AES SPECTRUM FROM THE TUBE EXPOSED TO THE HEAT EXCHANGER ENVIRONMENT FOR ONE MONTH THE MOST PROMINENT PEAKS ARE INDICATED

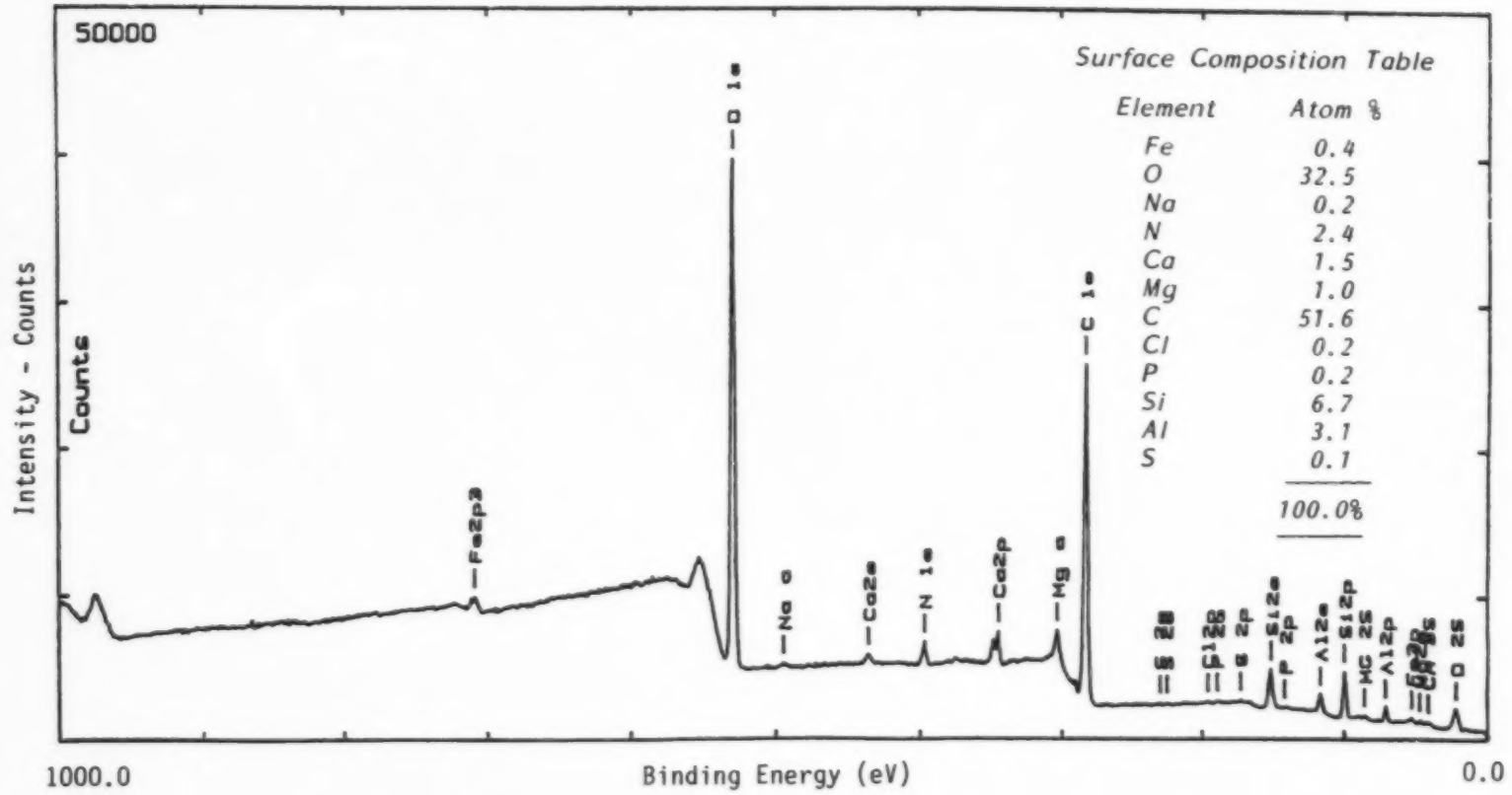
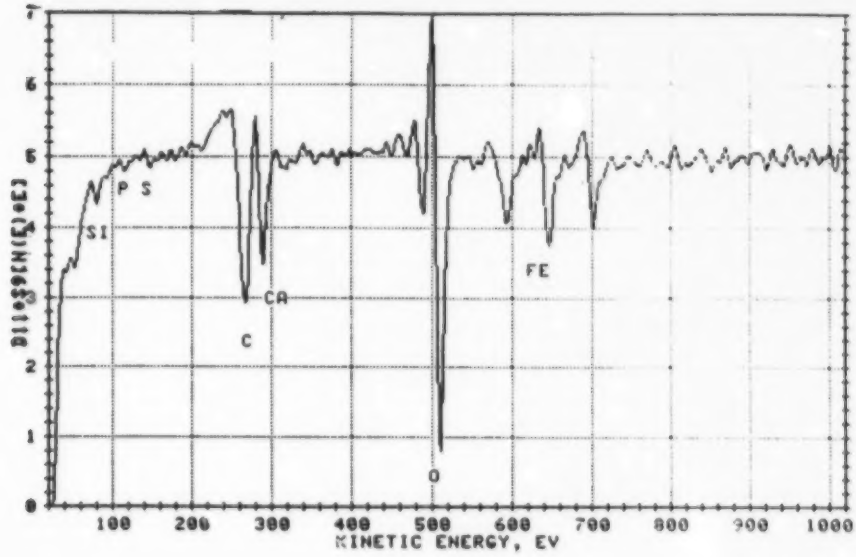
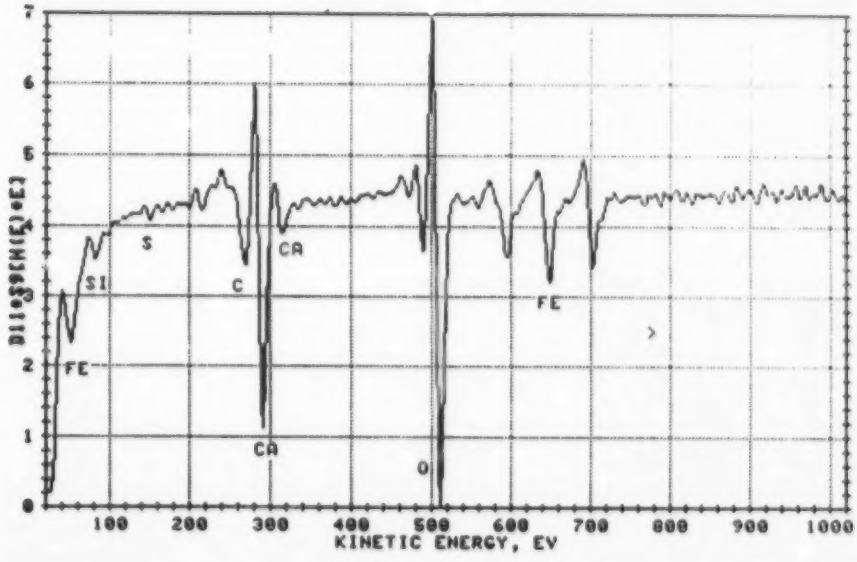


FIGURE 6

AN XPS BROAD SCAN FROM THE TUBE EXPOSED TO THE HEAT EXCHANGER ENVIRONMENT FOR TWO MONTHS



(a) Before sputtering



(b) After the removal of ≃ 150Å of material (1 minute sputtering)

FIGURE 7 a-b

AES SPECTRUM FROM THE TUBE EXPOSED TO THE HEAT EXCHANGER ENVIRONMENT FOR TWO MONTHS THE MOST PROMINENT PEAKS ARE INDICATED

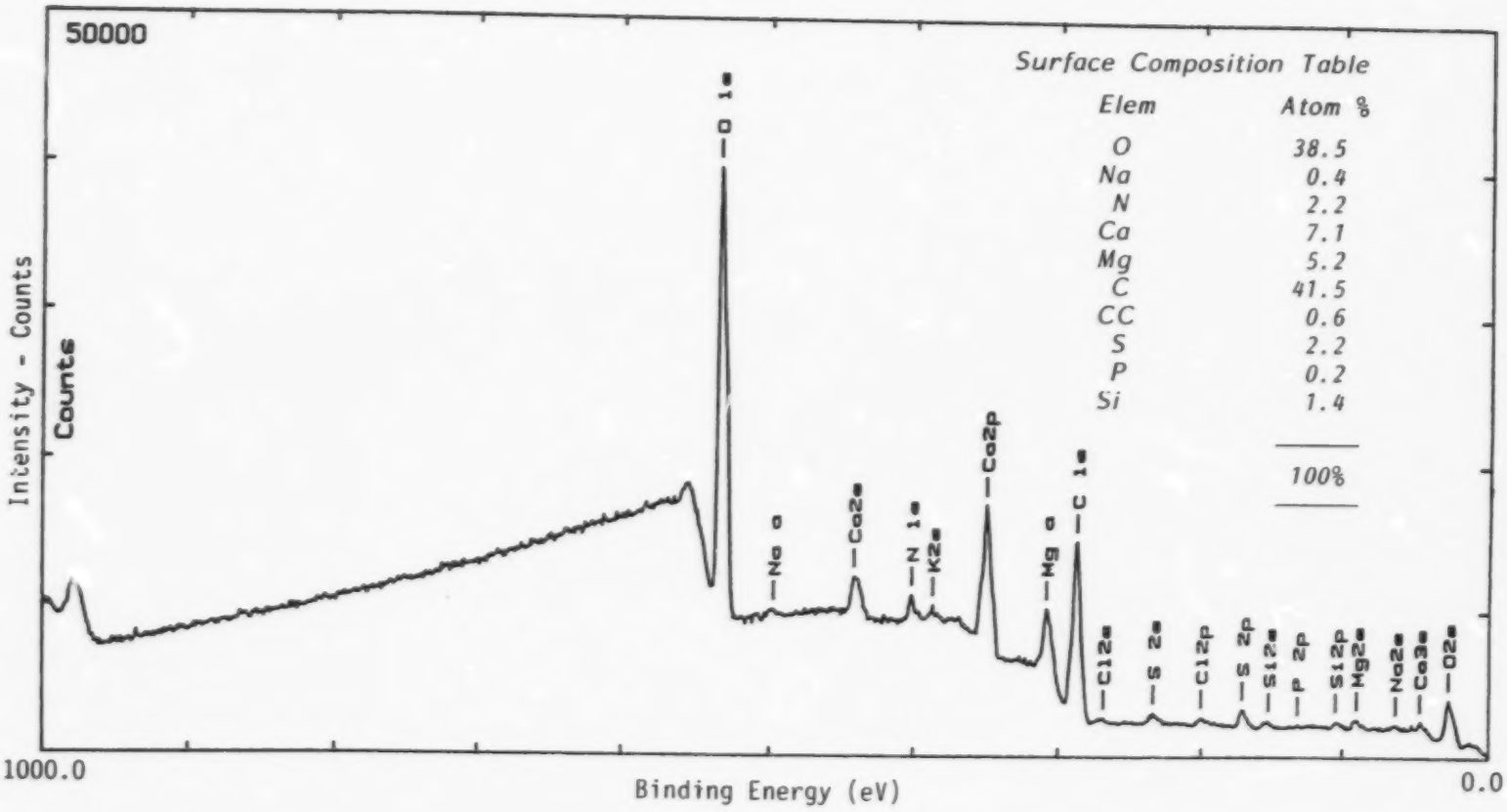


FIGURE 8

AN XPS BROAD SCAN FROM THE
TUBE EXPOSED TO THE HEAT EXCHANGER
ENVIRONMENT FOR FOURTEEN MONTHS

90-115

132759-RD

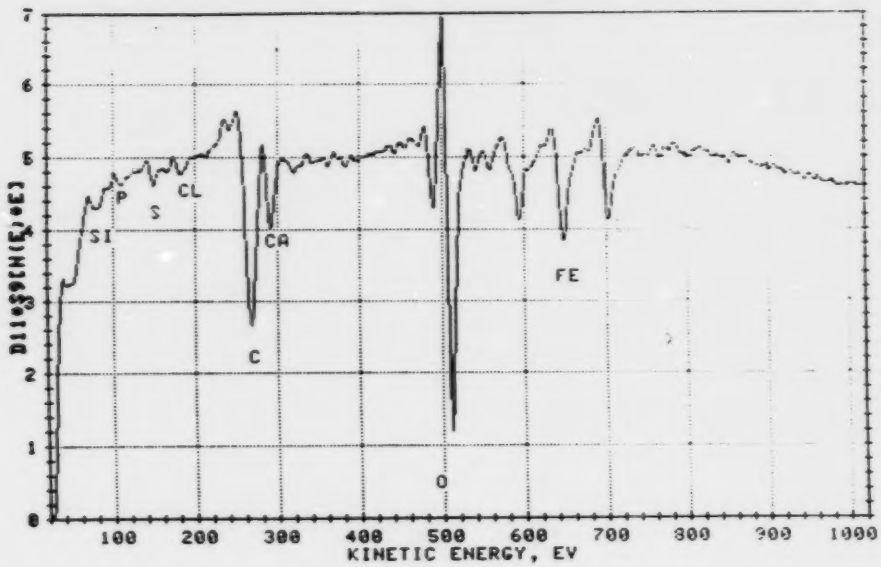


FIGURE 9

AES SPECTRUM FROM THE PIT REGION,
NOTE THE PRESENCE OF P, S, AND Cl

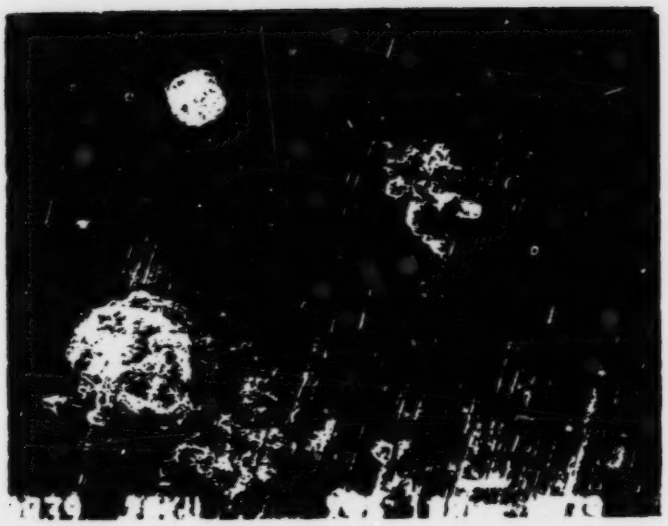


Figure 10

A general view of one of the pits observed after fourteen months of exposure.

Figure 11

A view of the interior of a pit. Pitting is clearly highly crystallographic.

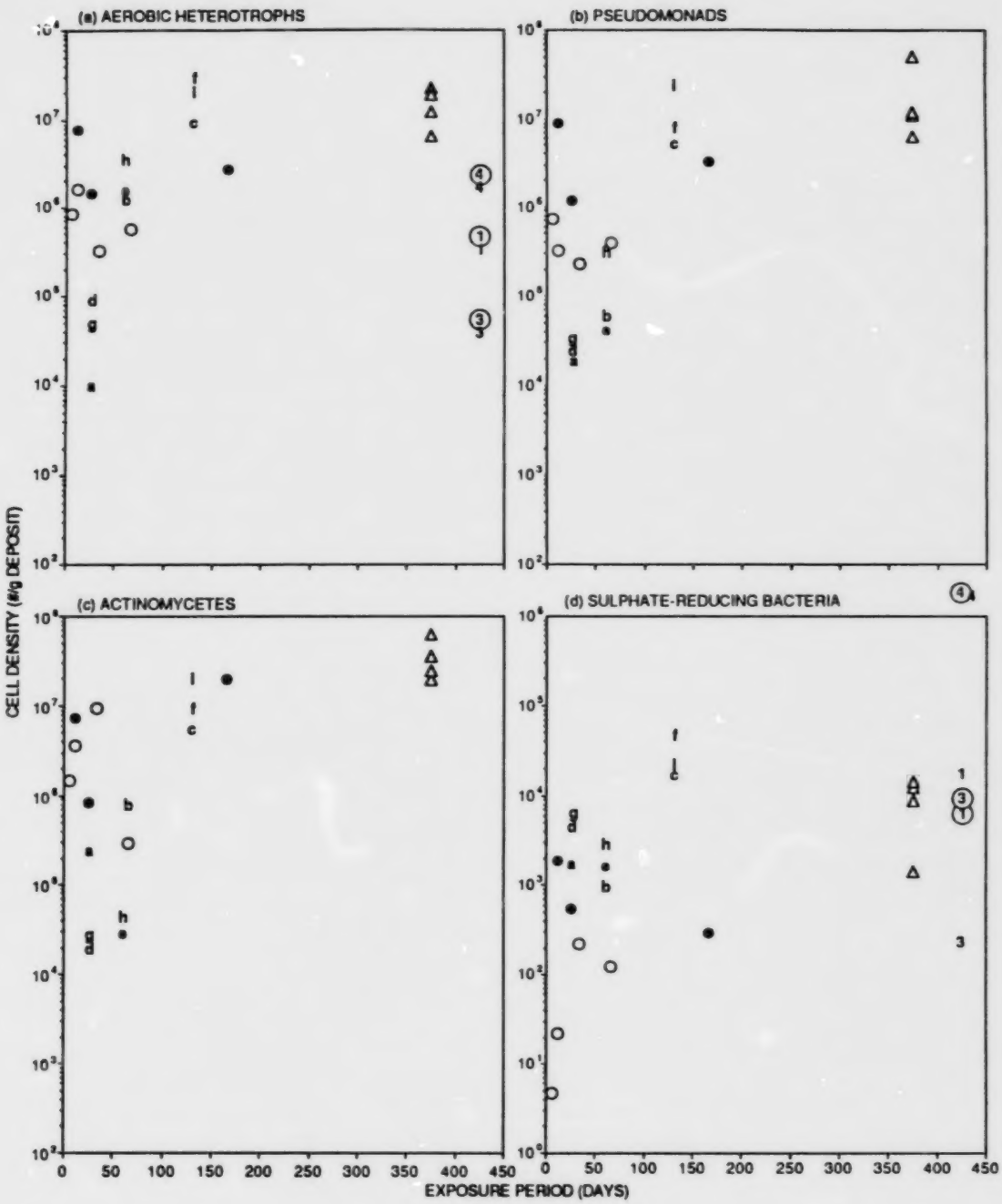


Figure 12

ABUNDANCE (#/g DEPOSIT) OF (a) AEROBIC HETEROTROPHS, (b) PSEUDOMONADS, (c) ACTINOMYCETES AND (d) SULPHATE-REDUCING BACTERIA WITHIN BIOFOULED SURFACES FROM TEST RIG AND LABORATORY IMMERSION STUDIES

LEGEND: TEST RIG STUDIES - △ DARLINGTON, ● PICKERING (1987) AND ○ PICKERING (1988) IMMERSSION STUDIES - a TO l (OHRDR 84-276-K). a - c \LAKE HURON (BRUCE) WATER; d - f LAKE ERIE (NANTICOKE) WATER; g - l LAKE ONTARIO (PICKERING) WATER ON 304L SS - 1,3 & (OHRDR CB86-3-K) 1 BIOFILM + SILICA; 3 BIOFILM ONLY 4 BIOFILM + LAKE DEPOSIT UNDER OXYGENATED OR STAGNANT (CIRCLED #'S) CONDITIONS FOR NO8800